

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 1 055 704 A2

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
29.11.2000 Bulletin 2000/48

(51) Int. Cl.⁷: **C08K 5/37**

(21) Application number: 00304092.0

(22) Date of filing: 15.05.2000

(84) Designated Contracting States:
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE**
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: 26.05.1999 US 320304

(71) Applicant: **ROHM AND HAAS COMPANY**
Philadelphia, Pennsylvania 19106-2399 (US)

(72) Inventors:
• Duvall, Tod Charles
West Chester, Ohio 45069 (US)
• Carpenter, Jeffrey Lynn
Cincinnati, Ohio 45245 (US)

(74) Representative:
Buckley, Guy Julian
ROHM AND HAAS (UK) LTD.
European Operations Patent Department
Lennig House
2 Mason's Avenue
Croydon CR9 3NB (GB)

(54) **Method for improving adhesion of water based inks to halogen containing resin articles**

(57) Flexible and semi-rigid vinyl chloride resin compositions comprising a combination of a latent mercaptan and a zinc salt of oxidized polyethylene (a zinc ionomer) as a heat stabilizer are substantially free from the offensive odor typically associated with mercaptans and are protected during processing by the degradation products of the latent mercaptan and the zinc ionomer. The oxidized polyethylene is split out from the ionomer to act as an adhesion promoter for aqueous inks and paints, and the residual zinc carboxylate functions as a co-stabilizer with the latent mercaptan in the composition. The latent mercaptan is exemplified by a 2-S-(tetrahydropyranyl)thioalkanol, a carboxylic acid ester thereof, a 2-S-(tetrahydropyranyl)thiocarboxylic acid, an ester thereof, and the furanyl homologs of each.

EP 1 055 704 A2

Description

FIELD OF THE INVENTION

- 5 [0001] This invention relates to improved adhesion of water-based inks and paints to articles made from heat stabilized halogen-containing resins. It relates particularly to articles of manufacture such as flexible film and semi-rigid tubing that are prepared from heat-stabilized vinyl chloride polymers.

BACKGROUND OF THE INVENTION

10

[0002] Changes in heat stabilizers and in printing inks over the years has resulted in a loss of printability of flexible poly (vinyl chloride) substrates. The curtailment of heavy metals (e.g. cadmium) in stabilizers and of volatile solvents in both stabilizers and printing inks has been held responsible for the loss of printability. Thus, there has arisen a need for a way to enhance the wettability of such present day PVC substrates.

- 15 [0003] A patent application by Witco Corporation published under the number WO96/15186 teaches that the wettability of heat-stabilized PVC film to water-based inks and the adherence of such inks to the film are improved by the incorporation of oxidized polyethylene in the PVC composition. The heat stabilizer is a mixture of barium and zinc carboxylates having up to 20 carbon atoms in combination with organic phosphites.

- 20 [0004] The surface tension of a heavy metal-containing PVC has been found to be from 25 to 33% higher than that of a traditionally plasticized PVC according to E.R. Napoleon in "Journal of Vinyl & Additive Technology", 3, No. 2, 145 (June 1997).

- [0005] As taught in co-pending, commonly assigned patent application Serial No. 09/133,605, filed August 13, 1998, the teachings of which are incorporated herein by reference, the degradation products of a blocked or latent mercaptan present during processing of the halogen-containing resin at an elevated temperature enhance the activity of metal-based heat stabilizers such as organotin carboxylates and mercaptides in the composition. Vinyl chloride resin compositions and articles made thereof are stabilized particularly well by a combination of very low levels of zinc carboxylates and latent mercaptans selected from the group consisting of 2-S-(hydroxyalkylthio)tetrahydropyran, 5-S-(hydroxyalkylthio)tetrahydrofuran, 6-S-(2-formylhydroxyalkylthio)tetrahydropyran, the carboxylic acid esters of said alcohols, and mixtures of said alcohols and esters. Said latent mercaptans are also referred to as 2-S-(tetrahydropyranyl)-thioalkanol; 2-S-(tetrahydropyranyl)thioalkyl carboxylate; 6-S-(2-formyl-tetrahydropyranyl)thioalkanol and carboxylates thereof, and their furanyl homologs, i.e., 5-S-(tetrahydrofuran)thioalkanol, and 5-S-(tetrahydrofuran)thioalkyl carboxylate.

SUMMARY OF THE INVENTION

35

[0006] It has now been found that a combination of such a latent mercaptan and a zinc salt of oxidized polyethylene is particularly valuable in that it imparts improved hydrophilicity to the surfaces of articles made from vinyl chloride resins as well as thermal stability during high temperature processing during fabrication of such articles. The zinc salt is the only metal-containing stabilizer present during the high temperature processing.

- 40 [0007] It is an object of this invention, therefore, to provide a heat stabilizer composition which is free from metals other than zinc and which also improves the wettability of vinyl chloride resins by water-based inks and paints.

[0008] It is another object of this invention to provide a heavy metal-free, heat stabilized halogen-containing resin having a surface tension which is amenable to coating with a water-based ink or paint.

- 45 [0009] It is a related object of this invention to provide heat stabilized flexible, semi-rigid, and rigid PVC resin articles which have improved receptivity to water-based inks and paints.

[0010] It is a related object of this invention to provide novel latent mercaptans which are useful, alone or in combination with other additives, in heat stabilizer compositions.

- [0011] These and other objects of the invention which will become apparent from the following description are achieved by adding a heavy metal-free heat stabilizer comprising a latent mercaptan and a synergistic amount of a zinc salt of oxidized polyethylene as the sole metal-containing stabilizer to a vinyl chloride resin and processing the resulting composition at the incipient resin decomposition temperature whereupon a small but hydrophilically effective amount of oxidized polyethylene is split from the zinc salt by liberated hydrogen chloride and the latent mercaptan degrades to liberate a free mercaptan. Examples of the latent mercaptan include, without limitation, 2-S-(tetrahydropyranyl)thioalkanol, a carboxylate thereof, a 2-S-(tetrahydropyranyl)thiocarboxylic acid or ester thereof, furanyl homologs of each, and mixtures thereof.

- 55 [0012] For the purposes of this invention, the terms blocked mercaptan and latent mercaptan are used interchangeably to mean a thioether which degrades during processing of the composition at an elevated temperature to liberate a free mercaptan.

[0013] Other products of the degradation of the blocked mercaptan are believed to include carbocations of the blocking moiety which are stabilized by a molecular structure in which the electron deficiency is shared by several groups. Resonance stabilization and neighboring group stabilization are two of the possible mechanisms by which the carbocations may be stabilized. The carbocations act as intermediates in the formation of stable compounds early in the hot processing of halogen-containing polymers. Although such mechanisms and the resultant carbocations are believed to be an impetus for the liberation of the active free mercaptan, this invention is in no way limited by the foregoing attempt to explain the working of the invention. Those skilled in the art will see the resonance stabilization and neighboring group stabilization that are possible in the following structures of the blocked mercaptan; other mechanisms may be at work in other blocked mercaptans represented by these structures that also liberate an active free mercaptan upon thermal and/or chemical degradation during processing of polymeric compositions containing such blocked mercaptans.

DETAILED DESCRIPTION OF THE INVENTION

[0014] The vinyl chloride resins, also referred to hereinafter as PVC resins, are made from monomers consisting of vinyl chloride alone or a mixture of monomers comprising, preferably, at least about 70% by weight of vinyl chloride, based on the total monomer weight. Examples of the copolymers include those made from vinyl chloride and from about 1 to about 30% of a copolymerizable ethylenically unsaturated material such as vinyl acetate, vinyl butyrate, vinyl benzoate, vinylidene chloride, diethyl fumarate, diethyl maleate, other alkyl fumarates and maleates, vinyl propionate, methyl acrylate, 2-ethylhexyl acrylate, butyl acrylate and other alkyl acrylates, methyl methacrylate, ethyl methacrylate, butyl methacrylate and other alkyl methacrylates, methyl alpha-chloroacrylate, styrene, trichloroethylene, vinyl ketones such as vinyl methyl ketone and vinyl phenyl ketone, 1-fluoro-2-chloroethylene, acrylonitrile, chloroacrylonitrile, allylidene diacetate, chloroallylidene diacetate, and vinyl ethers such as vinyl ethyl ether, vinyl chloroethyl ether, vinyl phenyl ether, and the vinyl ether of ethoxytetrahydropyran prepared by the reaction of one mole of acrolein with one mole of ethylene glycol divinyl ether. Typical copolymers include vinyl chloride-vinyl acetate (96:4 sold commercially as VYNW), vinyl chloride-vinyl acetate (87:13), vinyl chloride-vinyl acetate-maleic anhydride (86:13:1), vinyl chloride-vinylidene chloride (95:5); vinyl chloride-diethyl fumarate (95:5), and vinyl chloride 2-ethylhexyl acrylate (80:20).

[0015] As used herein, the term PVC composition means a composition comprising a vinyl chloride resin. A rigid PVC composition is one which does not contain a plasticizer. A semi-rigid PVC composition is one which contains from 1 to about 25 parts of a plasticizer per 100 parts by weight of the vinyl chloride resin. A flexible PVC composition contains from about 25 to about 100 parts per 100 parts by weight (phr) of the vinyl chloride resin. Alkyl esters of carboxylic acids in which there are from 1 to 3 alkyl groups having from 8 to 12 carbon atoms are representative of the plasticizers. The alkyl group may be n-octyl, 2-ethylhexyl, nonyl, decyl, or dodecyl. Suitable esters include phthalates, trimellitates, benzoates, adipates, glutarates, and sebacates. The plasticizer may also be a pentaerythritol or such an ester thereof. A polymeric plasticizer is also suitable.

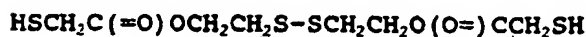
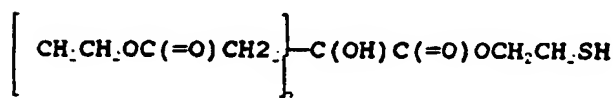
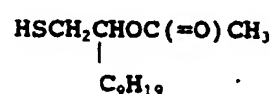
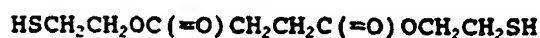
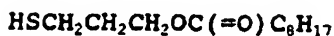
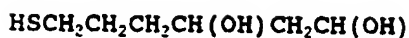
[0016] As used herein, an acyloxyalkyl radical originates from a carboxylic acid ester of an alkyl alcohol. Therefore, the R¹ radical of the stearic acid ester of mercaptopropanol, as represented by the formula below, is the stearyloxypropyl radical; likewise, the R¹ radical of the oleic acid ester of mercaptopropanol, which is one of the tallate esters of that alcohol, is the oleoyloxypropyl radical.

[0017] As used herein, substantially means largely if not wholly that which is specified but so close that the difference is insignificant.

[0018] One of the advantages of this invention is that the offensive odor of mercaptans is masked by a blocking group so that the latent mercaptan thus created may be put into a PVC composition or the like with little or no offense to the operator with the knowledge that the free mercaptan will be released as a degradation product when the treated composition is heated during the usual processing, e.g. extrusion. It is believed that the free mercaptan is consumed as it is liberated in response to the evolution of hydrogen chloride at the incipient decomposition temperature of the vinyl chloride resin.

[0019] The blocking compounds are preferably those which are capable of furnishing a stabilized carbocation having a molecular structure in which the electron deficiency is shared by several groups. Resonance stabilization and neighboring group stabilization are two of the possible mechanisms by which the carbocations may be stabilized. Blocking compounds such as 3,4-dihydropyran and 2,3-dihydrofuran are preferred for the purposes of this invention.

[0020] The blocked mercaptans suitable for the purposes of this invention are represented by the following formula:



[0024] In general, the procedure for making the latent mercaptans which are useful in this invention comprises adding the mercapto group of the free mercaptan across the double bond of a polarized, unsaturated compound as follows:

[0025] To a stirred mixture, under nitrogen atmosphere, of the mercaptan, acid catalyst, and optionally, a small percentage of antioxidant to inhibit radical reactions, is added dropwise to the polarized, unsaturated compound, either neat or in solution, while maintaining the temperature between 10-70° C. The mixture or solution is then heated for between 1 and 6 hours at 35°-70° C and conversion to product is monitored by gas chromatography and iodine titration for SH. The acid catalyst is removed by an alkaline wash and the resulting product is dried with magnesium sulfate and filtered. The solvent, if required, is removed under reduced pressure at <50° C to yield the latent mercaptan. A solid phase catalyst may be used and then filtered out of the reaction mixture and regenerated for use in a subsequent synthesis. In this way, a wash step is eliminated. This generalized procedure is referred to hereinafter as Procedure A.

[0026] In accordance with Procedure A, for example, mercaptoethanol is added across the double bond of N-vinylcaprolactam to yield N-2-hydroxyethylthioethylcaprolactam. Mercaptoethyldecanoate (or mercaptoethylcaproate) reacts with 3,4-dihydropyran in that procedure to give 2-S-(tetrahydropyranyl)thioethyldecanoate. Bis(hydroxyethylthioethyl) cyclohexyl ether is made from the mercaptoethanol and cyclohexyl di-vinyl ether. In like manner, the corresponding caprate, oleate, and tallate esters form the corresponding cyclohexyl ethers. Also, indene is converted by the addition of the mercaptoethanol to 2H-dihydroindenylthio-ethanol.

[0027] A generalized procedure for the condensation of a free mercaptan with a labile halogen-containing compound is as follows:

[0028] To a stirred mixture of the mercaptan and halogen-containing compound under nitrogen atmosphere is added dropwise a solution of sodium methoxide in methanol while maintaining the temperature below 50° C. Optionally, the reaction is allowed to proceed without the addition of a base source and the liberated hydrogen chloride is removed by nitrogen gas sweep and neutralized with the use of an external acid scrubber. The mixture or solution is then heated for between 2 to 24 hours at 50°-70° C and conversion to product is monitored by gas chromatography and iodine titration for %SH. The product is then neutralized, washed with water, dried with magnesium sulfate, and filtered. The solvent, if required, is removed under reduced pressure at <50° C to yield the latent mercaptan. This generalized procedure is referred to hereinafter as Procedure B.

[0029] A generalized procedure for the condensation of a free mercaptan with a labile hydroxyl-containing compound is as follows:

[0030] To a stirred solution of the mercaptan, acid catalyst, and solvent under nitrogen atmosphere is added the

hydroxy-containing compound either neat or in solution while maintaining the temperature <45° C. The solution is then heated to 45°-75° C for between 1 to 10 hours and conversion to product is monitored by gas chromatography and iodine titration for %SH. Optionally, an azeotropic solvent is chosen for removal of reaction water by an appropriate means at reflux temperatures, typically 60°-120° C. Completion of reaction is achieved after the theory amount of water has been collected. The acid catalyst is removed by alkaline wash and the resulting solution is dried with magnesium sulfate and filtered. The solvent is removed under reduced pressure at <55° C to yield the latent mercaptan. This procedure is referred to hereinafter as Procedure C.

[0031] For example, 2-hydroxybenzyl alcohol condenses with mercaptoethanol in accordance with Procedure C to form 1-(2-hydroxyphenyl)-1-S-(2-hydroxyethylthio)methane.

[0032] A generalized procedure for the reaction of a free mercaptan with a glycidyl ether is as follows:

[0033] To a stirred mixture of the mercaptan and acid catalyst under nitrogen atmosphere is added the glycidyl ether, either neat or in solution, while maintaining the temperature between 25°-60° C. The mixture or solution is then heated to between 50°-75° C for a period of 1 to 6 hours and conversion to product is monitored by gas chromatography and iodine titration for %SH. The acid catalyst is removed by alkaline wash, the resulting product is dried with magnesium sulfate, and filtered. The solvent, if required, is removed under reduced pressure at <55° C to yield the latent mercaptan. For example, the reaction between mercaptoethanol and glycidyl neodecanoate gives $C_9H_{19}C(=O)OCH_2CH(OH)CH_2SCH_2CH_2OH$. This procedure is referred to hereinafter as Procedure D.

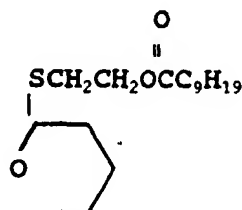
[0034] A generalized procedure for the condensation of a free mercaptan with an aldehyde is as follows:

[0035] To a stirred solution of the mercaptan, acid catalyst, and azeotropic solvent under nitrogen atmosphere is added the aldehyde with heating to reflux, typically between 65°-120° C, for removal of reaction water. Completion of reaction is achieved after the theory amount of water has been collected. Optionally, to a stirred solution of mercaptan, aldehyde, and ether is added BF_3 -etherate dropwise under reflux conditions. The solution is refluxed for between 1 to 6 hours and conversion to product is monitored by gas chromatography. The acid catalyst is removed by alkaline wash, the solution is dried with magnesium sulfate and filtered. The solvent is removed under reduced pressure at <65° C to yield the latent mercaptan. This generalized procedure is referred to hereinafter as Procedure E.

[0036] The polarized, unsaturated compounds are exemplified by 3,4-dihydropyran; 3,4-dihydro-2-methoxy-2H-pyran; 3,4-dihydro-2-ethoxy-2H-pyran; 3,4-dihydro-2-methoxy-2H-pyran; 3,4-dihydro-2-formyl-2H-pyran; 3,4-dihydro-3-methoxy-2H-pyran; and 2,3-dihydrofuran. The 3,4-dihydro-2-formyl-2H-pyran is made by the Diels-Alder dimerization of acrolein at high temperatures and pressures. The 3,4-dihydro-2-alkoxy-2H-pyrans and 3,4-dihydro-2-phenoxy-2H-pyran are made by the reaction of the corresponding vinyl ether with acrolein in the presence of a catalytic amount of a zinc salt, e.g., zinc chloride. A variety of 3,4-dihydro-2H-pyrans having a substituent in the 2-position can be made by similar reactions. The products formed by the reaction of 1 and 2 moles of acrolein with the divinyl ether of an alkylene- or polyalkylene glycol are blocking agents, also. In the case of the reaction of two moles of acrolein per mole of a divinyl ether, latent mercaptans made from the resulting di-(3,4-dihydropyran) ethers also have the potential of being chelating agents in the polymer compositions of this invention. The reaction of one mole of acrolein with one mole of the divinyl ether forms a monomer which may be copolymerized with vinyl chloride with or without a wide variety of ethylenically unsaturated compounds. The product from the reaction of acrolein with chloroethyl vinyl ether provides a substituted 3,4-dihydropyran that can be further derivatized.

A stabilizer composition of this invention may be made quite conveniently by the addition of a mercaptan across the double bond of the pyran ring in the presence of zinc chloride as a catalyst for the addition and as a synergistic stabilizer in the product.

[0037] Examples of 2-S-(tetrahydropyranyl)thioalkanols that are suitable as latent mercaptans for this invention include, without limitation, 2-S-(tetrahydropyranyl)thioethanol, 2-S-(tetrahydropyranyl)thiopropanol, and 2-S-(tetrahydropyranyl)thiobutanol 6-S-(2-formyl-tetrahydropyranyl)thioethanol, and their furanyl homologs, e.g., 5-S-(tetrahydrofuran)thioalkanol. The carboxylates suitable for the purposes of this invention are exemplified by 2-S-(tetrahydropyranyl)thioethyl caprate, which also may be named 2-S-(2-decanoyloxyethylthio) tetrahydropyran, made by the reaction between mercaptoethyl caprate and 3,4-dihydropyran according to the foregoing procedure and has the following formula:



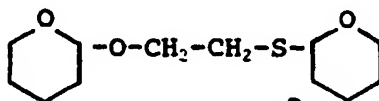
[0038] Homologs of the thus described compounds which are particularly useful in the stabilization of flexible PVC compositions include the 2-S-(tetrahydropyranyl)thioalkyl carboxylates and their furanyl homologs wherein the ethyl moiety is replaced by propyl, butyl, hexyl, and others in the series up to and including dodecyl and the capric acid radical of said compound is replaced by other fatty acid radicals (saturated and unsaturated) or resin acid radicals having up to and including 22 carbon atoms. The acids are exemplified by caproic, caprylic, lauric, myristic, palmitic, stearic, arachidic, behenic, and the oleic and linoleic acids, as such, or as found in tall oil acids along with abietic and pimaric acids. The mercaptoalkyl carboxylate moiety is thus exemplified by mercaptoethyl laurate, mercaptoethyl oleate, mercaptoethyl hexanoate, mercaptoethyl octanoate, mercaptoethyl myristate, mercaptoethyl palmitate, mercaptoethyl stearate, mercaptoethyl oleate, mercaptoethyl linoleate, and the mercaptopropyl, mercaptobutyl, and mercaptooctyl homologs of each of the above. The esters are made by the conventional method of reacting the hydroxyl group of a mercaptoalkanol with the desired carboxylic acid in the presence of an acidic catalyst and removing water as it forms.

[0039] When 2-S-tetrahydropyranythioethanol is prepared from 3,4-dihydropyran by said procedure, by-products having the following formulas are also obtained:

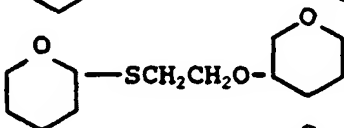
15



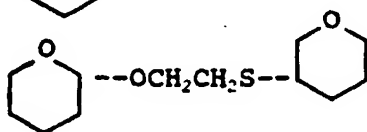
20



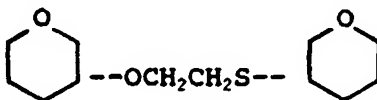
25



30

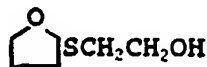


35



[0040] The homologous by-products are expected when 2,3-dihydrofuran is reacted with mercaptoethanol but the principal product is the 5-S-tetrahydrofuranythioethanol shown by the following structure:

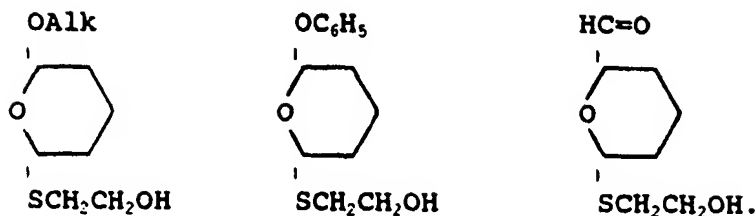
45



[0041] When the 3,4-dihydropyran is replaced by a 3,4-dihydro-2-alkoxy-pyran; a 3,4-dihydro-2-phenoxy-pyran; or a 3,4-dihydro-2-formyl-pyran in the above procedure, the following products are formed:

55

5



10

[0042] A 2-S-(tetrahydropyranyl)mercaptoalkyl carboxylate is more active as a heat stabilizer in flexible PVC compositions than the tetrahydropyranyl-blocked mercaptans derived from alkylmercaptans such as dodecanethiol when activated according to this invention as manifest in the improved color hold properties and dynamic thermal stability of such stabilized PVC compositions. The higher activity may be the result of the better compatibility of the ester-containing latent mercaptans with a plasticized PVC. The compatibility of the corresponding homologous furan-based latent mercaptans is similar.

[0043] As used herein, a zinc ionomer is defined as a salt in which both of the zinc valences are paired with carboxylate anions from the oxidized polyethylene, a mixed salt in which one of the zinc valences is paired with a carboxylate ion having from 7 to 18 carbon atoms and the other is paired with a carboxylate ion from an oxidized polyethylene, or a physical mixture of a zinc salt of a carboxylic acid having from 7 to 18 carbon atoms and a zinc salt an oxidized polyethylene. For the purposes of this invention, the oxidized polyethylene has a molecular weight of at least about 750 and up to about 2100. The oxidized polyethylenes have from about 50 to about 150 carbon atoms and are believed to have hydroxyl and ketonic substituents along the polymer chain as well as carboxylic groups. The acid number ranges from about 2 to about 50. The melting point of the oxidized polyethylene is preferably from about 60°C to 150°C (140-302°F) so that it is solid at the temperatures at which vinyl chloride resins are normally used. A preferred oxidized polyethylene, sold by Allied-Signal Corp. as AC629A, has molecular weight of about 2000, a softening point in the 213-221°F (101-105°C) range, and an acid number of 14-17.

[0044] The carboxylic acids that are useful along with the oxidized polyethylene may be aliphatic, arylaliphatic, aromatic, or alkylaromatic; the aliphatic moieties have a straight or branched chain structure and may be saturated or unsaturated. Thus, the mixed salt may include an anion from, for example, heptanoic, octanoic (or caprylic), 2-ethylhexanoic, decanoic (or capric), lauric, oleic, stearic, benzoic, phenylacetic, or methylbenzoic acid. An ionomer wherein the octanoate and the oxidized polyethylene fulfill the zinc valences is an example of a preferred latent wetting agent for the vinyl chloride resin.

[0045] The stoichiometric amount of zinc oxide, zinc chloride, or a zinc carboxylate/chloride is reacted with the oxidized polyethylene to prepare the desired zinc salt. The zinc carboxylate/chloride is prepared from zinc chloride and less than the stoichiometric amount of the desired carboxylic acid so that the remaining chloride ions may react with the oxidized polyethylene to form a mixed salt as an ionomer useful in this invention. An ionomer is also made by the stepwise reaction of the zinc oxide with the oxidized polyethylene and, for example, octanoic acid or by a one step reaction with a mixture of the oxidized polyethylene and octanoic acid.

[0046] The adhesion promoting stabilizer compositions of this invention consist essentially of from about 40 % to about 98 %, preferably from about 60 % to about 80 % of a latent mercaptan and from about 2 to about 60 %, preferably from about 20 to about 40 %, of the zinc ionomer, based on the total weight of the stabilizer composition. The latent mercaptan is exemplified by 2-S-(tetrahydropyranyl)thioalkanol, a carboxylate thereof, a 2-S-(tetrahydrofuran-yl)-thioalkanol, a carboxylate thereof, a 2-S-(tetrahydropyranyl)thiocarboxylic acid, an ester thereof, a 2-S-(tetrahydrofuran-yl)thiocarboxylic acid, an ester thereof, and a mixture of two or more of said alkanols, acids, and esters. They are particularly suited to impart superior stabilization against the deteriorative effects of heat and ultra-violet light on flexible PVC resins in comparison with stabilizer compositions previously known in the art. They may be prepared by blending the components thereof in any convenient manner which produces a homogeneous mixture, such as by shaking or stirring in a container. Likewise, the stabilizer compositions of this invention can be incorporated in a vinyl chloride resin in an appropriate mill or mixer or by any other of the well-known methods which provide uniform distribution of the stabilizer throughout the polymer composition.

[0047] It will be readily apparent to one of ordinary skill in the art, that the precise amount of stabilizer composition added to the vinyl chloride resin will depend upon several factors, including, but not limited to, the particular resin employed, the temperature to which the resin will be subjected, and the possible presence of other stabilizing compounds. In general, the more severe the conditions to which the resin is subjected, and the longer the term required for resisting degradation, the greater will be the amount of stabilizer composition required. Generally, the stabilizer composition is used in an amount to provide as little as about 0.20 part and as much as about 5 parts by weight of the latent

mercaptan per hundred parts by weight (phr) of the PVC resin. While there is no critical upper limit to the amount of latent mercaptan which can be employed, amounts up to about 3.0 phr of the PVC resin are preferred. The zinc salt of oxidized polyethylene is used in an amount effective to improve the wettability to water-based paints and inks of an article formed from the vinyl chloride resin. From about 0.2 to about 2.5 phr is suitable, but from 0.5-1.5 phr is preferable.

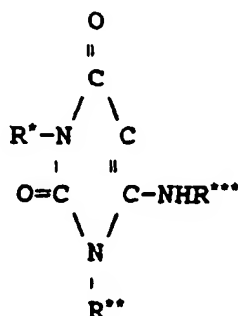
[0048] In addition to the stabilizer compositions of this invention, the PVC resin compositions of this invention may contain plasticizers, as mentioned above in regard to semi-rigid and flexible PVC, as well as pigments, fillers, antioxidants, blowing agents, dyes, ultraviolet light absorbing agents, densifying agents, biocides, and the like.

[0049] Conventional non-metallic stabilizers can also be included in the PVC resin compositions of the present invention. Thus, there can be included 0.01-0.75 %, based on the weight of the resin, of sulfur containing compounds such as dilauryl-thiodipropionate, distearyl 3,3'-thiodipropionate, dicyclohexyl-3,3'-thiodipropionate, dioleoyl-3,3'-thiodipropionate, dibenzyl-3,3'-thiodipropionate, didecyl-3,3'-thiodipropionate, dibenzyl-3,3'-thiodipropionate, diethyl-3,3'-thiodipropionate, lauryl ester of 3-methylmercaptopropionic acid, lauryl ester of 3-butylmercaptopropionic acid, lauryl ester of 3-lauryl mercaptopropionic acid, and phenyl ester of 3-octyl mercaptopropionic acid.

[0050] Likewise there can be included from 0.01-10% by weight of the vinyl chloride polymer of a polyol stabilizer for vinyl chloride resins. Thus there can be included glycerol, sorbitol, pentaerythritol, mannitol and polyethers such as diethylene glycol, triethylene glycol, tetraethylene glycol, tripropylene glycol, and the like.

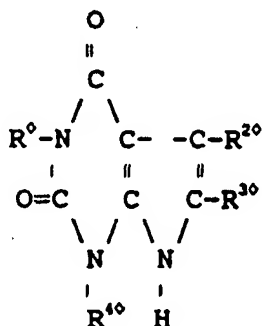
[0051] Nitrogen containing stabilizers such as dicyandiamide, melamine, urea, formoguanamine, dimethyl hydantoin, guanidine, thio-urea, 2-phenylindoles, aminocrotonates, N-substituted maleimides, uracil, the 1,3-dialkyl-6-amino-uracil derivatives described in German Offenlegungsschrift 19,741,778 by Ciba Specialty Chemicals Holding Inc., and the pyrrolodiazine diones described in published Australian Patent Application No. AU-A-48232/96 by Ciba-Geigy, and the like may also be included in the compositions of this invention in amounts of 0.1-10% by weight.

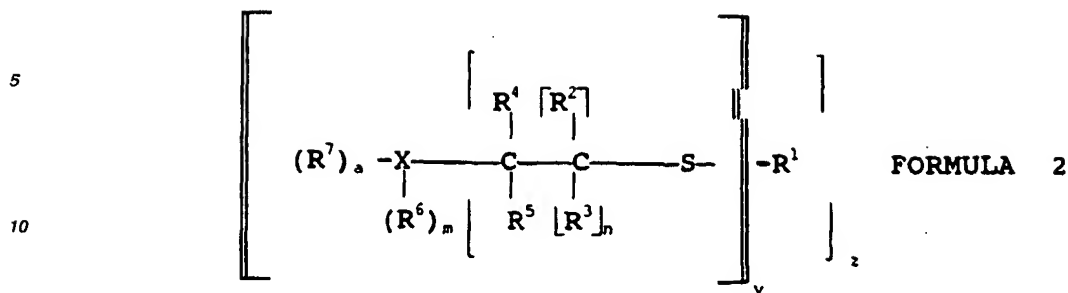
[0052] The 1,3-dialkyl-6-amino-uracils and 1,3-dialkyl-6-phenylamino uracils are prepared by known methods such as those taught in U.S. Patent No. 2,598,936, which is incorporated herein by reference. Other uracils suitable for use in this invention have substituents such as hydroxyalkyl, alkoxyalkyl, hydroxyphenyl, etc. and are taught in U.S. Patent No. 4,656,209, which is incorporated herein by reference, also. They, also, may be made according to the procedures of the '936 patent. Their structure is illustrated by the following formula:



wherein R*, and R**, are independently hydrogen, alkyl, hydroxyalkyl, or alkoxyalkyl, and R*** is hydrogen, alkyl, phenyl, or hydroxyphenyl, wherein each of the alkyl moieties have from 1 to 4 carbon atoms.

[0053] Of particular interest are the pyrrolodiazine diones described by the formula:

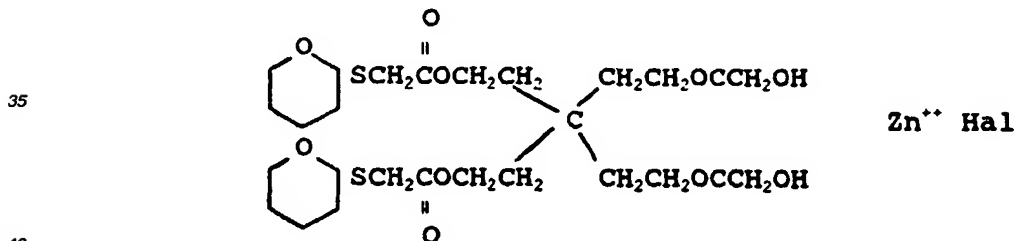




15 wherein a is 0 or 1, m is 0 or 1, and n is 0 or 1; y = 1 to 4, when y = 1, z is 1 to 4, when y is more than 1 z is 1; R¹ is R'C(O)OH wherein R' is an alkylene radical, or R¹ is a thio-[bis(alkoxyacyl)], dithio-[bis(alkoxyacyl)], pentaerythrityl, alkenyloxy(polyalkoxy)alkyl, oxy[bis(alkoxyacyl)], oxy[bis(polyalkoxyacyl)], benzyloxy(polyalkoxy)alkyl, or benzyloxy(polyalkoxy)acyl radical, said alkyl, alkylene, and acyl radicals having from 1 to 22 carbon atoms; R², R³, R⁴, R⁵, R⁶, and R⁷ are independently hydrogen, a hydroxyl, mercapto, alkyl, alkylene, acyl, aryl, haloaryl, alkaryl, aralkyl, hydroxyalkyl, chloroalkoxy, alkylene, alkenyloxyalkoxy, alkoxy, aryloxy, alkaryloxy, mercaptoalkyl, hydroxyalkylmercaptoalkyl, mercaptoalkylene, hydroxyaryl, alkoxyaryl, alkoxyhydroxyaryl, arylcarbonyl, or mercaptoaryl radical having from 1 to 22 carbon atoms; X is aryl, haloaryl, alkaryl, hydroxyaryl, dihydroxyaryl, aralkaryl, alkoxyaryl, arylcycloalkyl, or a heteroatom selected from the group consisting of oxygen and sulfur, with the option that one or both of the R³ and R⁵ alkylene radicals joins with R⁷ and X to form a heterocyclic moiety with X as the heteroatom.

25 **[0060]** It has also been found that a one-component PVC stabilizer is obtained from the latent mercaptans of Formula 1 and Formula 2 wherein R¹ is pentaerythrityl by forming a complex with a zinc halide. For example, a zinc halide forms a complex with a pair of neighboring hydroxyl groups in a latent mercaptan such as the adduct of 2 moles of 3,4-dihydropyran with one mole of the diester of pentaerythrityl and a mercaptocarboxylic acid such as thioglycolic acid or mercaptopropionic acid. The one-component PVC stabilizer is pre-formed or formed *in situ* by complexing a zinc halide, preferably the chloride, with such a latent mercaptan as shown by the following formula:

30



wherein Hal is a halogen ion, preferably a chloride ion. The preparation of blocked mercaptans and zinc salts used in the adhesion promoting stabilizers of this invention, the preparation of said stabilizers, and the advantages of compositions comprising said stabilizers are illustrated as follows.

45

Preparation of 2-S-(tetrahydropyranyl)thioethylcaprate

50 **[0061]** ¹H-NMR spectroscopy was used to determine the molecular structure of 2-S-(decanoyloxyethylthio)tetrahydropyran or 2-S-(tetrahydropyranyl)thioethylcaprate which was prepared by adding 42.0 grams (0.50 mole) of 3,4-dihydropyran to 112.2 grams (0.50 equivalent) of mercaptoethylcaprate (14.7% SH) in the presence of an acid catalyst over a period of 45 minutes while maintaining a nitrogen atmosphere and a temperature below 35 °C and then heating it to 50°C and holding that temperature for 1.5 hours. After cooling the solution, it was washed with two 200 ml portions of a 10 % sodium bicarbonate solution in water, followed by a 200 ml wash with water. The organic layer was dried with

55 MgSO₄ to yield a light yellow liquid having an SH content of less than 0.5 percent as determined by titration with a 0.100 N iodine solution in isopropanol. The ¹H-NMR (CDCl₃, δ) spectrum was: 2.3 (2H, t, -C(=O)-CH₂-CH₂), 2.8 (2H, m, -S-CH₂-CH₂-), 4.2 (2H, m, -S-CH₂-CH₂-O-), 4.9 (1H, m, -O-CH(-S-CH₂-)-CH₂-CH₂-). The total color change (dE) of a PVC composition containing 0.13 phr of the latent mercaptan of this example was measured versus a white tile standard

using a Hunter colorimeter at one minute intervals. At one minute, it was 4.2; at five minutes, it was 8.4.

Preparation of 2-S-tetrahydropyranyl) thioethyltallate

[0062] 2-S-tetrahydropyranyl) thioethyltallate was prepared by adding 172.45 grams (2.05 equiv.) of 3,4-dihydro(2H)pyran dropwise to 760.00 grams (2.00 equiv.) of 2-mercaptoethyltallate (8.70% SH by iodometric titration) containing 0.93 gram of methanesulfonic acid (70% active) over a period of 45 minutes under a nitrogen blanket and a temperature between 25-35°C and heating to 35-40°C for 2 hours. After cooling the solution, 3 grams of Norite carbon black was charged and the product was vacuum filtered to yield 932 grams of yellow liquid having a SH content of less than 0.4% as determined by titration with 0.100 N iodine solution in isopropanol. The ¹H-NMR(CDC13, δ) spectrum was: 2.3 (2H, t, -C(=O)-CH₂-CH₂-), 2.8 (2H, m, -S-CH₂-CH₂-), 4.3 (2H, m, (-CC(=O)-O-CH₂), 4.9 (1H, m, -O-CH(-S-CH₂)-CH₂-CH₂-). GC of the product (1% in ether) indicated one primary product peak at 26.3 minutes retention time (50-300°C; 10°C/min.; split flow injector/FID). The product is referred to in Table 1 below as DHP/2-MET.

Preparation of a Zinc Ionomer

[0063] To a 250 ml flask fitted with a side-arm condenser there was charged with stirring 50 grams (0.0143 equivalent) of oxidized polyethylene (Allied Signal AC-629A), 175 ml of butyl carbitol, 1.16 grams (0.0286 equivalent) of 99% pure zinc oxide, and 2.06 grams (0.0143 equivalent) of 99% pure octanoic acid. The reaction mixture was then heated to 75°C (167°F) and 3 drops of glacial acetic acid were added before the temperature was raised to 120-125°C (248-257°F) for 20 minutes. The mixture was stripped of water and solvent by applying a vacuum of 3 mm Hg at that temperature. The product is a cream-colored wax which has a zinc content of 1.8 % (measured as the metal) according to atomic absorption analysis. The theoretical zinc content is 1.8%. The product is referred below as ZNION.

Example 1

[0064] A mixture of 5.2 grams of the above zinc ionomer and 20.8 grams of 2-S-tetrahydropyranyl-thioethyl tallate was heated in a 50 ml Erlenmeyer flask to 85°C to obtain a homogeneous dispersion. When cooled, the product is a soft paste having a zinc content of 0.4% as the metal. The product is referred to in Table below as ZNPM#1.

Example 2

[0065] A general flexible PVC composition containing:

INGREDIENT	AMOUNT
PVC resin (k=70)	100.0 parts
Dioctyl phthalate	40.0 phr
Epoxidized soybean oil	5.0 phr
Stearic acid	0.2 phr
Stabilizer	See Table 1

was processed on a dynamic two-roll mill (roll speeds 30R/40R) at 350°F with chips taken at five minute intervals to a maximum of 60 minutes. The yellowness index of the chips was measured using a Hunter Labs Colorimeter (L, a, b) for comparison in Table II. The dynamic thermal stability (DTS) of the compositions was measured on a Brabender Plastimeter PL-2100 rheometer at 200°C/80rpm with No. 6 roller blades and an electric head. The DTS, shown in Table 3, was recorded as the elapsed time in minutes before a sharp upturn in the torque curve during processing was observed. The DTS value is considered to be the time at which degradation of the PVC began.

TABLE 1

Example	Stabilizer	Amount (phr)
2	ZNPM#1	2.5

EP 1 055 704 A2

TABLE 1 (continued)

Example	Stabilizer	Amount (phr)
3	DHP/2-MET	2.0
	and ZNION added separately	0.5
Control #1	DHP/2-MET	2.5
Control #2	ZNION	0.5
Comp Ex 1	AKZO INTERSTAB CZ-11	2.5
Comp Ex 2	FERRO THERM-CHEK 760X	2.5

TABLE 2

PVC Color Hold (Yellowness Index) Minutes												
Time/ Ex.	5	10	15	20	25	30	35	40	45	50	55	60
2	11.8	13.9	17.1	19.3	20.0	23.1	26.0	30.9	33.1	36.3	41.6	49.5
3	11.5	12.8	13.4	15.4	16.6	17.8	22.3	27.0	31.6	35.9	44.4	52.8
Con 1	46.5	78.7	87.8	89.9	88.6	91.8	99.1	101.9	106.7	105.2	113.5	112.1
Con 2	21.8	27.2	35.6	45.0	59.2	80.9	84.7	burn	--	--	--	--
CE 1	13.4	19.7	25.3	33.2	37.7	66.9	74.7	burn	--	--	--	--
CE 2	13.5	16.2	21.3	27.9	38.5	burn	--	--	--	--	--	--

Table 3

Dynamic Thermal Stability	
Example	Time/minutes
2	45.9
3	44.6
Con 1	55.1
Con 2	14.0
CE 1	25.7
CE 2	12.6

EXAMPLE 4

[0066] A general flexible PVC formulation containing:

INGREDIENT	AMOUNT
PVC resin (k=70)	100.0 parts
Diocetyl phthalate	40.0 phr
Epoxidized soybean oil	5.0 phr
Stearic acid	0.2 phr
Stabilizer	See Table 4

was processed on a dynamic two-roll mill at 350°F to give a series of 45 mil thick sheets. A drop of a material having a known surface tension was placed on each sheet and the advancing contact angle of each drop was quantified with a goniometer at 24°C. The cosine of the contact angle was plotted against the surface tension of each drop. The line was extrapolated to cosine = 1 (critical surface tension). The results are given in Table 5 where Sheets A-E were made from the formulations shown in Table 4.

TABLE 4

Example	Stabilizer	Amount (phr)	% metal
Comp Ex 3 Sheet A	DHP/2-MET	2.00	0.0
	Zinc octanoate (18% Zn)	0.05	0.5
Example 5 Sheet B	DHP/2-MET	2.00	0.5
	ZNION	0.75	
Comp Ex 4 Sheet C	Calcium stearate	2.00	0.5
	Zinc octanoate (18% Zn)	0.05	0.5
Comp Ex 5 Sheet D	Commercial Ba/Zn/P	2.00	9.0
Comp Ex 6 Sheet E	Commercial Ca/Zn	2.00	3.0

Table 5

PVC Sheet	Surface tension (± 0.5 dyne-cm)
A	22.0
B	25.6
C	22.0
D	21.3
E	21.2

[0067] It can be seen that the stabilizer/adhesion promoter of this invention imparts an increase in the surface tension to the vinyl sheets. This 20% increase in hydrophilicity makes the vinyl sheets more amenable to coating with

water-based inks.

[0068] The following examples show the utility in this invention of latent mercaptans of Formula 1 wherein R¹ is a radical from an ester of a glycol.

5 EXAMPLE 6

Preparation of Intermediate

[0069] A mixture of 736.16 grams (8 moles) of thioglycolic acid, 848.96 grams (8 moles) of diethyleneglycol, and
 10 1.3 grams of p-toluene sulfonic acid was heated to 80°C at a pressure of 400 Torr in a reactor equipped with a mechanical stirrer, a thermometer, and a vacuum take-off condenser. The refluxing temperature was held for 1 hour before the pressure was reduced to 120 Torr over a period of 2.5 hours to remove water formed by the esterification. The temperature rose to 120°C as the pressure was further reduced to 20 Torr over a period of 0.5 hour. The total weight of water removed was 140.92 grams. The product has an acid value of 12 and an SH content of 16.75% by weight. The yield
 15 was 1421.12 grams. The product was a mixture of the diethyleneglycol mono- and diesters of thioglycolic acid (i.e., hydroxyethoxyethylmercaptoacetate and ethoxyethyl di-mercaptoacetate) and was satisfactory.

Preparation of Adduct

[0070] To the 1421 grams (7.89 equivalents) of intermediate thus produced there was added 6.38 grams of
 20 AMBERLYST 15 ion exchange resin and then 708.21 grams (8.42 equivalents) of 3,4-dihydro(2H)pyran (DHP) was added dropwise over a period of 135 minutes under a nitrogen blanket at a temperature 40-50°C. After continued heating at 40-50°C for 2.25 hours, the %SH was 5.36. Another charge of DHP weighing 300.21 grams (about 3.5 moles) was added during a period of 0.5 hour and the reaction mixture was held at about 55°C for 0.5 hour to reduce the %SH
 25 to 3.32. After standing overnight (about 14 hours) under nitrogen, the product had an SH content of 2.68 %.

[0071] The product was a mixture containing 2-S-(tetrahydropyranyl) hydroxyethoxyethoxyethylthioglycolate, wherein R¹ is hydroxyethoxyethoxyacetylmethyl, and bis-[2-S-(tetrahydropyranyl)ethoxyethyl] thioglycolate, wherein R¹ is oxy[bis(ethoxyacetylmethyl)] and y is 2.

30 Preparation of Stabilizer

[0072] Said adduct and the zinc ionomer (or ZNION) described above are mixed to form an adhesion promoting stabilizer of this invention.

35 Example 7

Preparation of intermediate

[0073] A mixture of 98.23 grams (1.07 moles) of thioglycolic acid, 160.06 grams (1.07 moles) of triethyleneglycol,
 40 and 0.2 gram of p-toluene sulfonic acid was heated to 100°C at a pressure of 250 Torr in a reactor equipped with a mechanical stirrer, a thermometer, and a vacuum take-off condenser. The refluxing temperature was held for 25 minutes before the pressure was reduced to 10 Torr over a period of 1.5 hours to remove water formed by the esterification. The product contained the triethyleneglycol monoester (about 57% of the total weight) and the triethyleneglycol diester of thioglycolic acid (about 20 %) and was satisfactory.

Preparation of Adduct

[0074] A mixture containing (2-S-tetrahydropyranyl) hydroxyethoxyethoxyethylthioglycolate and bis-(2-S-tetrahydropyranyl)-ethoxyethoxyethyl di-thioglycolate was prepared by cooling 100 grams (0.42 equivalent of SH) of the thus
 50 prepared mixture of triethyleneglycol mono- and diesters of thioglycolic acid along with 0.2 gram of AMBERLYST 15 ion exchange resin to 0°C and adding 39.18 grams (0.462 mole) of DHP dropwise over a period of 30 minutes. The mixture was held at 0°C for 1 hour and then heated gradually to room temperature (about 22°C) and held there for 2 hours. The yield of product was 139.2 grams and the SH content was 3.5%.

55 Preparation of Stabilizer

[0075] Said adduct and the zinc ionomer (or ZNION) described above are mixed to form an adhesion promoting stabilizer of this invention.

Example 8*Preparation of Intermediate*

- 5 [0076] A mixture of 92.0 grams (1 mole) of thioglycolic acid, 212.21 grams (2 moles) of diethyleneglycol, and 0.24 gram of p-toluene sulfonic acid was heated to 100°C at a pressure of 200 Torr in a reactor equipped with a mechanical stirrer, a thermometer, and a vacuum take-off condenser. The temperature was held for 0.5 hour before the pressure was reduced to 10 Torr over a period of 1.9 hours and then held for 70 minutes to remove water formed by the esterification. The temperature was raised to 110°C as the pressure was further reduced to less than 1 Torr over a period and held for 3 hours. The diethyleneglycol mono-ester of thioglycolic acid constituted 85.9 % and the diester constituted 14.1 % of the weight of the product. The SH content of the product was 19.49% by weight, which was satisfactory.

Preparation of Adduct

- 15 [0077] A mixture of 70 grams (0.412 equivalent) of the intermediate thus produced and 0.15 gram of AMBERLYST 15 ion exchange resin was cooled to less than 0.5°C and then 36.52 grams (0.434 equivalent) of DHP was added dropwise over a period of about 7 minutes and after 3 hours it was warmed to room temperature (about 22°C).

Preparation of Stabilizer

- 20 [0078] Said adduct and the zinc ionomer (or ZNION) described above are mixed to form an adhesion promoting stabilizer of this invention.

Example 9

- 25 Preparation of Intermediate

- [0079] A mixture of 188.85 grams (2.05 moles) of thioglycolic acid, 154.26 grams (1.0 mole) of dithiodiglycol, and 5.1 grams of p-toluene sulfonic acid was heated to 110°C in a nitrogen atmosphere for 2.5 hours in a reactor equipped with a mechanical stirrer, a thermometer, and a vacuum take-off condenser to remove about 32 mls of water formed by the esterification. The SH content of the product was 20.6 %. The theoretical SH content of the dithiodiglycol diester of thioglycolic acid is 21.9%.

Preparation of Adduct

- 35 [0080] A mixture of 15 grams (0.091 equivalent) of the intermediate thus produced and 8.04 grams (0.096 equivalent) of DHP was stirred and 1 drop of 70% methane sulfonic acid caused an exothermic reaction which raised the temperature to 89°C before cooling lowered it to 40°C. The material was diluted with tetrahydrofuran and stripped at 35°C/2mm Hg for 1 hour to give a product whose SH content was less than 0.1% and an acid number of 4.2.

Preparation of Stabilizer

- 40 [0081] Said adduct and the zinc ionomer (or ZNION) described above are mixed to form an adhesion promoting stabilizer of this invention.

Example 10Preparation of Intermediate

- 50 [0082] A mixture of 69.30 grams (0.752 mole) of thioglycolic acid, 50 grams (0.367 mole) of pentaerythritol and 1.25 grams of p-toluene sulfonic acid was heated to 100°C in a vacuum of about 200 mm Hg to remove water formed by the esterification. After 60 minutes, a gas chromatograph showed that the predominant product was the diester of thioglycolic acid and was satisfactory. The removal of water was finished at 15 mm Hg.

Preparation of Adduct

- 55 [0083] The general procedure of Example 9 is followed to give the desired oxy-bis(2-S-tetrahydropyranylthioglycolate) of pentaerythritol wherein R¹ of Formula 1 above is pentaerythritol and y is 2.

Preparation of Stabilizer

[0084] Said adduct and the zinc ionomer (or ZNION) described above are mixed to form an adhesion promoting stabilizer of this invention.

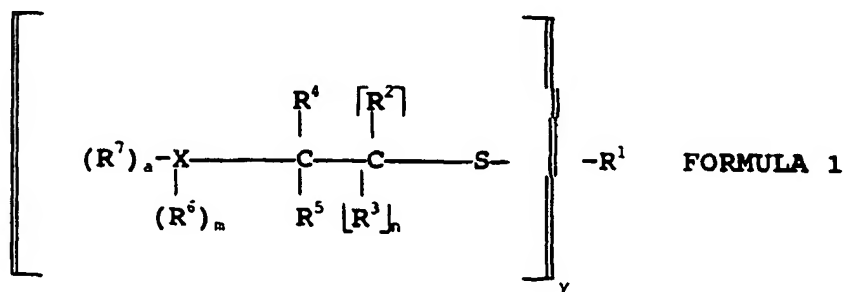
[0085] The two hydroxyl groups of the thioglycolate may be complexed with the zinc ion of a zinc halide to form a non-adhesion promoting heat stabilizer for a halogen-containing polymer. Said stabilizer may, however, be mixed with the adhesion-promoting stabilizer as another embodiment of the invention claimed herein.

[0086] Articles of manufacture contemplated by this invention, e.g. packaging film and tubing are formed from the stabilized compositions of this invention by any of the well-known conventional techniques for forming polymers into shaped articles.

[0087] While a few specific embodiments of this invention have been disclosed in considerable detail, variations and modifications of these embodiments can be effected without departing from the spirit and scope of the invention as disclosed and claimed herein.

Claims

1. A heavy metal-free, heat-stable PVC resin composition comprising a blocked mercaptan having the structure:

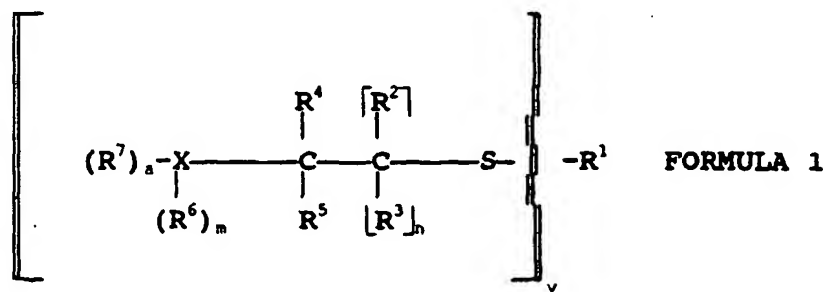


wherein a is 1, m is 0, and n is 0 or 1; y = 1 to 4; R¹ is R'C(O)OH, wherein R' is an alkylene radical having 2 or 3 carbon atoms, or R¹ is an alkyl, pentaerythrityl, alkylene, cycloalkyl, cycloalkylene, aryl, alkaryl, aralkyl, aralkylene, hydroxyalkyl, dihydroxyalkyl, alkoxyalkyl, acyloxyalkyl, hydroxy(polyalkoxy)alkyl, hydroxy(polyalkoxy)acyl, acyloxy(hydroxyalkyl), acyloxy(alkoxyalkyl), acyloxy(polyalkoxy)alkyl, acyloxy(polyalkoxy)acyl, alkoxyacyl, oxy[bis(alkoxyacyl)], oxy[bis(polyalkoxyacyl)], benzoyloxy(polyalkoxy)alkyl, benzoyloxy(polyalkoxy)acyl, or alkylene bis-(acyloxyalkyl), thio-bis-[alkoxyacyl], dithio-bis-[alkoxyacyl], alkoxy(polyalkoxy)acyl, hydroxyalkoxyalkyl, alkoxy(hydroxyalkyl), alkoxy(polyalkoxy)alkyl, mercaptoalkyl, mercaptoalkylene, mercaptoalkoxyacyl, tetrahydropyranyloxy(polyalkoxy)acyl, tetrahydropyranyloxyalkyl, hydroxyaryl, or mercaptoaryl radical having from 1 to 22 carbon atoms; R², R³, R⁴, R⁵, R⁶, and R⁷ are independently hydrogen, a hydroxyl, mercapto, alkyl, alkylene, acyl, aryl, haloaryl, alkaryl, aralkyl, hydroxyalkyl, alkenyloxyalkoxy, alkoxy, aryloxy, alkaryloxy, mercaptoalkyl, hydroxyalkyl/mercaptoalkyl, mercaptoalkylene, hydroxyaryl, alkoxyaryl, alkoxyhydroxyaryl, arylcarbonyl, or mercaptoaryl radical having from 1 to 22 carbon atoms; X is a heteroatom selected from the group consisting of oxygen and sulfur, and one or both of the R³ and R⁵ alkylene radicals joins with R⁷ and X to form a heterocyclic moiety with X as the heteroatom; and

as the sole metal-containing stabilizer, an amount of a zinc ionomer effective to improve the wettability by water-based paints and inks of an article formed from the PVC resin composition.

2. The composition of claim 1 wherein X is oxygen and the resin is a flexible poly (vinyl chloride).
3. The composition of claim 2 wherein R¹ is acyloxyalkyl.
4. The composition of claim 3 wherein R¹ is acyloxyethyl.
5. The composition of claim 2 wherein the zinc ionomer is a mixed salt of a carboxylic acid having from 7 to 18 carbon atoms and an oxidized polyethylene.

6. The composition of claim 3 wherein the zinc salt is a mixed salt of a carboxylic acid having from 7 to 18 carbon atoms and an oxidized polyethylene.
7. The composition of claim 3 wherein the acyloxy group contains from 12 to 18 carbon atoms.
8. The composition of claim 1 wherein the amount of the zinc ionomer is from about 0.2 to about 2.5 parts per hundred parts by weight of the resin.
9. The composition of claim 8 wherein the zinc ionomer is a mixed salt of a carboxylic acid having from 7 to 18 carbon atoms and an oxidized polyethylene.
10. The composition of claim 1 wherein the heterocyclic moiety is tetrahydropyranyl.
11. The composition of claim 1 wherein the heterocyclic moiety is tetrahydrofuranyl.
12. The composition of claim 3 wherein the heterocyclic moiety is tetrahydropyranyl.
13. The composition of claim 1 wherein the zinc ionomer comprises an oxidized polyethylene having a molecular weight of at least about 750.
14. The composition of claim 3 wherein the zinc ionomer comprises an oxidized polyethylene having a molecular weight of at least about 750.
15. The composition of claim 2 wherein R^1 is acyloxyethyl, the acyloxy moiety contains from 12 to 18 carbon atoms, the zinc ionomer is a mixed salt of a carboxylic acid having from 7 to 18 carbon atoms and an oxidized polyethylene having a molecular weight of at least about 750 and an acid number of from about 2 to about 50, the amount of the zinc ionomer is from about 0.5 to about 1.5 phr, and the heterocyclic moiety is tetrahydropyranyl.
16. A heavy metal-free stabilizer for a poly(vinyl chloride) resin consisting essentially of from about 40 % to about 80% by weight of a blocked mercaptan having the formula:

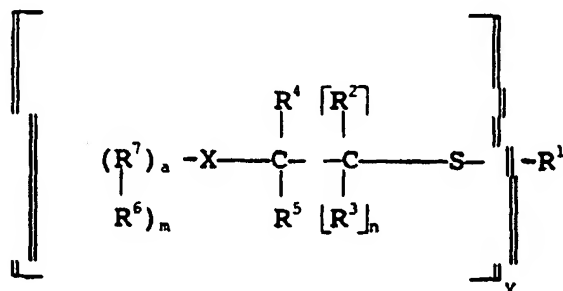


wherein a is 1, m is 0, and n is 0 or 1; $y = 1$ to 4; R^1 is $R'C(O)OH$, wherein R' is an alkylene radical having 2 or 3 carbon atoms, or R^1 is an alkyl, pentaerythrityl, alkylene, cycloalkyl, cycloalkylene, aryl, alkaryl, aralkyl, aralkylene, hydroxyalkyl, dihydroxyalkyl, alkoxyalkyl, acyloxyalkyl, hydroxy(polyalkoxy)alkyl, hydroxy(polyalkoxy)acyl, acyloxy(hydroxyalkyl), acyloxy(alkoxyalkyl), acyloxy(polyalkoxy)alkyl, acyloxy(polyalkoxy)acyl, alkoxyacyl, oxy[bis(alkoxyacyl)], oxy[bis(polyalkoxyacyl)], benzoyloxy(polyalkoxy)alkyl, benzoyloxy(polyalkoxy)acyl, or alkylene bis-(acyloxyalkyl), thio-bis-[alkoxyacyl], dithio-bis-[alkoxyacyl], alkoxy(polyalkoxy)acyl, hydroxyalkoxyalkyl, alkoxy(hydroxyalkyl), alkoxy(polyalkoxy)alkyl, mercaptoalkyl, mercaptoalkylene, mercaptoalkoxyacyl, tetrahydropyranyloxy(polyalkoxy)acyl, tetrahydropyranyloxyalkyl, hydroxyaryl, or mercaptoaryl radical, said alkyl, alkylene, alkoxy, and acyl radicals having from 1 to 22 carbon atoms; R^2 , R^3 , R^4 , R^5 , R^6 , and R^7 are independently hydrogen, a hydroxyl, mercapto, alkyl, alkylene, acyl, aryl, haloaryl, alkaryl, aralkyl, hydroxyalkyl, alkenyloxyalkoxy, alkoxy, aryloxy, alkaryloxy, mercaptoalkyl, hydroxyalkylmercaptoalkyl, mercaptoalkylene, hydroxyaryl, alkoxyaryl, alkoxyhydroxyaryl, arylcarbonyl, or mercaptoaryl radical having from 1 to 22 carbon atoms; X is a heteroatom selected from the group consisting of oxygen and sulfur, and one or both of the R^3 and R^5 alkylene radicals joins with R^7 and X to form a heterocyclic moiety with X as the heteroatom; and

a zinc ionomer.

17. The stabilizer of claim 16 wherein R^1 is acyloxyethyl, the acyloxy moiety contains from 12 to 18 carbon atoms, the zinc ionomer comprises a mixed salt of a carboxylic acid having from 7 to 18 carbon atoms and an oxidized polyethylene having a molecular weight of at least about 750, X is oxygen, and the heterocyclic moiety is tetrahydropyranyl.

18. A method for improving the water wettability of a PVC article which comprises mixing a vinyl chloride resin with a latent mercaptan having the formula:



FORMULA 1

wherein a is 1, m is 0, and n is 0 or 1; y = 1 to 4; R^1 is $R'C(O)OH$, wherein R' is an alkylene radical having 2 or 3 carbon atoms, or R^1 is an alkyl, pentaerythrityl, alkylene, cycloalkyl, cycloalkylene, aryl, alkaryl, aralkyl, aralkylene, hydroxyalkyl, dihydroxyalkyl, alkoxyalkyl, acyloxyalkyl, hydroxy(polyalkoxy)alkyl, hydroxy(polyalkoxy)acyl, acyloxy(hydroxyalkyl), acyloxy(alkoxyalkyl), acyloxy(polyalkoxy)alkyl, acyloxy(polyalkoxy)acyl, alkoxyacyl, oxy[bis(alkoxyacyl)], oxy[bis(polyalkoxyacyl)], benzoyloxy(polyalkoxy)alkyl, benzoyloxy(polyalkoxy)acyl, or alkylene bis-(acyloxyalkyl), thio-bis-[alkoxyacyl], dithio-bis-[alkoxyacyl], alkoxy(polyalkoxy)acyl, hydroxyalkoxyalkyl, alkoxy(hydroxyalkyl), alkoxy(polyalkoxy)alkyl, mercaptoalkyl, mercaptoaryl radical having from 1 to 22 carbon atoms; R^2 , R^3 , R^4 , R^5 , R^6 , and R^7 are independently hydrogen, a hydroxyl, mercapto, alkyl, alkylene, acyl, aryl, haloaryl, alkaryl, aralkyl, hydroxyalkyl, alkenyloxyalkoxy, alkoxy, aryloxy, alkaryloxy, mercaptoalkyl, hydroxyalkylmercaptoalkyl, mercaptoalkylene, hydroxyaryl, alkoxyaryl, alkoxyhydroxyaryl, arylcarbonyl, or mercaptoaryl radical having from 1 to 22 carbon atoms; X is a heteroatom selected from the group consisting of oxygen and sulfur, and one or both of the R^3 and R^5 alkylene radicals joins with R^7 and X to form a heterocyclic moiety with X as the heteroatom;

with a zinc ionomer as the sole metal-containing stabilizer and heating the mixture to the incipient resin decomposition temperature.

19. The method of claim 18 wherein X is oxygen and R^1 is acyloxyalkyl.

20. The method of claim 18 wherein the zinc ionomer comprises a mixed salt of a carboxylic acid having from 7 to 18 carbon atoms and an oxidized polyethylene.

21. The method of claim 19 wherein the acyloxy moiety of the acyloxyalkyl group contains from 12 to 18 carbon atoms.

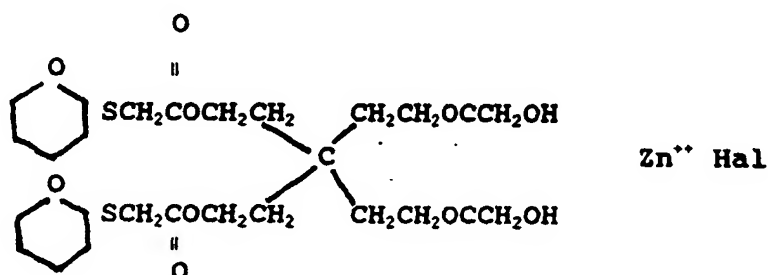
22. The method of claim 18 wherein the amount of the zinc ionomer is from about 0.2 to about 2.5 parts per hundred parts by weight of the resin.

23. The method of claim 22 wherein the zinc ionomer is a mixed salt of an oxidized polyethylene and a carboxylic acid having from 7 to 18 carbon atoms.

24. The method of claim 19 wherein the heterocyclic moiety is tetrahydropyranyl.

25. The method of claim 18 wherein the heterocyclic moiety is tetrahydrofuranlyl.

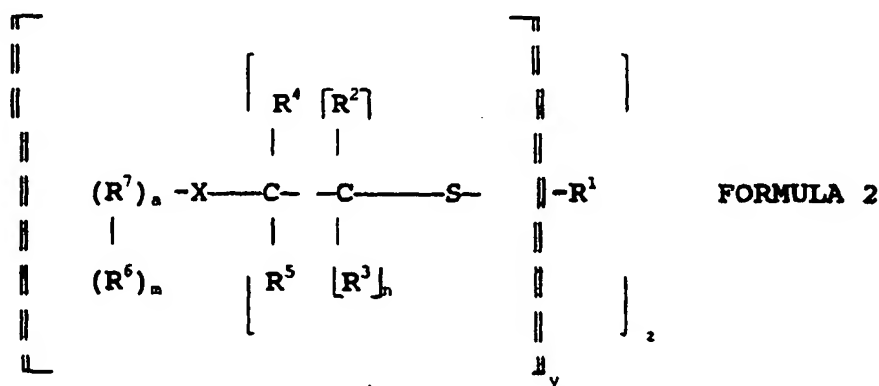
26. The method of claim 18 wherein the zinc ionomer comprises a mixed salt of an oxidized polyethylene having a molecular weight of from about 750 to about 2100 and an acid number of from about 2 to about 50.
27. The method of claim 19 wherein the zinc ionomer comprises a mixed salt of an oxidized polyethylene having a molecular weight of from about 750 to about 2100 and an acid number of from about 2 to about 50 and a carboxylic acid having from 7 to 18 carbon atoms.
28. The method of claim 19 wherein R^1 is acyloxyethyl in which the acyloxy moiety contains from 12 to 18 carbon atoms, the heterocyclic moiety is tetrahydropyranyl, the zinc ionomer is a mixed salt of a carboxylic acid having from 7 to 18 carbon atoms and an oxidized polyethylene having an acid number of from about 2 to about 50, and the amount of the zinc ionomer is from about 0.5 to about 1.5 phr.
29. A one-component PVC stabilizer consisting of a complex of a zinc salt with a latent mercaptan as shown by the following formu



la: wherein Hal represents a halide ion.

30. A PVC composition comprising the stabilizer of claim 29.

31. A latent mercaptan having the following formula:



wherein a is 0 or 1, m is 0 or 1, and n is 0 or 1; $y = 1$ to 4, when $y = 1$, z is 1 to 4, when y is more than 1 z is 1; R^1 is $R^1C(O)OH$ wherein R^1 is an alkylene radical having 2 or 3 carbon atoms, or R^1 is a thio-[bis(alkoxyacyl)], dithio-[bis(alkoxyacyl)], pentaerythrityl, alkenyloxy(polyalkoxy)alkyl, oxy[bis(alkoxyacyl)], oxy[bis(polyalkoxyacyl)], benzoyloxy(polyalkoxy)alkyl, or benzoyloxy(polyalkoxy)acyl radical, said alkyl, alkylene, and acyl radicals having from 1 to 22 carbon atoms; R^2 , R^3 , R^4 , R^5 , R^6 , and R^7 are independently hydrogen, a hydroxyl, mercapto, alkyl, alkylenyl, acyl, aryl, haloaryl, alkaryl, aralkyl, hydroxyalkyl, chloroalkoxy, alkylene, alkenyloxyalkoxy, alkoxy, aryloxy, alkaryloxy, mercaptoalkyl, hydroxyalkylmercaptoalkyl, mercaptoalkylenyl, hydroxyaryl, alkoxyaryl, alkoxyhydroxyaryl, arylcarbonyl, or mercaptoaryl radical having from 1 to 22 carbon atoms; X is aryl, haloaryl, alkaryl, hydroxyaryl, dihydroxyaryl, aralkaryl, alkoxyaryl, arylcycloalkyl, or a heteroatom selected from the group consisting of oxygen and sulfur, with the option that one or both of the R^3 and R^5 alkylenyl radicals joins with R^7 and X to form a hetero-

cyclic moiety with X as the heteroatom.

32. A zinc ionomer-free composition comprising a PVC resin and the latent mercaptan of claim 31.

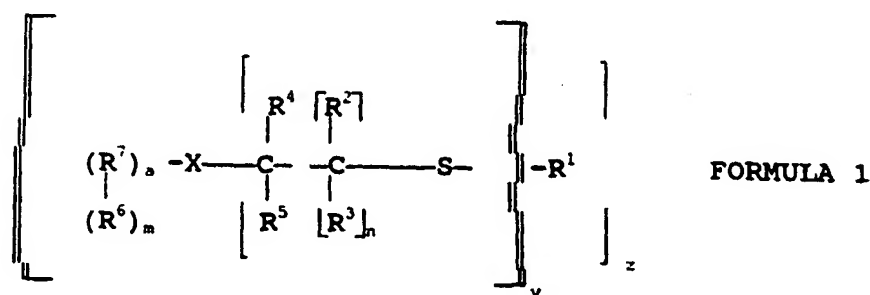
33. A zinc ionomer-free composition comprising a PVC resin, the latent mercaptan of claim 31, and from about 0.005 to less than 0.5 % of at least one synergist selected from the group consisting of a metallic-based heat stabilizer and a Lewis acid, based on the weight of the PVC resin.

34. A heat-stable PVC resin composition comprising a blocked mercaptan having the structure:

10

15

20



25

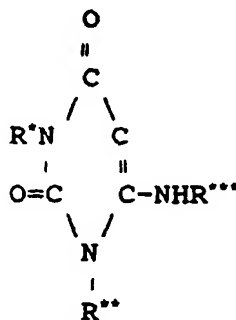
30

35

40

45

50



55

wherein R^* and R^{**} , are independently hydrogen, alkyl, hydroxyalkyl, or alkoxyalkyl, and R^{***} is hydrogen, alkyl, phenyl, or hydroxyphenyl, wherein each of the alkyl moieties have from 1 to 4 carbon atoms, and optionally,

as the sole metal-containing stabilizer, an amount of a zinc ionomer effective to improve the wettability by water-based paints and inks of an article formed from the PVC resin composition.



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) **EP 1 055 704 A3**

(12)

EUROPEAN PATENT APPLICATION

(88) Date of publication A3:
22.01.2003 Bulletin 2003/04

(51) Int Cl.7: **C08K 5/37, C08L 27/06,
C08K 5/098**

(43) Date of publication A2:
29.11.2000 Bulletin 2000/48

(21) Application number: 00304092.0

(22) Date of filing: 15.05.2000

(84) Designated Contracting States:
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE**
Designated Extension States:
AL LT LV MK RO SI

(72) Inventors:
• Duvall, Tod Charles
West Chester, Ohio 45069 (US)
• Carpenter, Jeffrey Lynn
Cincinnati, Ohio 45245 (US)

(30) Priority: 26.05.1999 US 320304

(74) Representative: Buckley, Guy Julian
ROHM AND HAAS (UK) LTD.
European Operations Patent Department
Lennig House
2 Mason's Avenue
Croydon CR9 3NB (GB)

(71) Applicant: **ROHM AND HAAS COMPANY**
Philadelphia, Pennsylvania 19106-2399 (US)

(54) **Method for improving adhesion of water based inks to halogen containing resin articles**

(57) Flexible and semi-rigid vinyl chloride resin compositions comprising a combination of a latent mercaptan and a zinc salt of oxidized polyethylene (a zinc ionomer) as a heat stabilizer are substantially free from the offensive odor typically associated with mercaptans and are protected during processing by the degradation products of the latent mercaptan and the zinc ionomer. The oxidized polyethylene is split out from the ionomer

to act as an adhesion promoter for aqueous inks and paints, and the residual zinc carboxylate functions as a co-stabilizer with the latent mercaptan in the composition. The latent mercaptan is exemplified by a 2-S-(tetrahydropyranyl)thioalkanol, a carboxylic acid ester thereof, a 2-S-(tetrahydropyranyl)thiocarboxylic acid, an ester thereof, and the furanyl homologs of each.

EP 1 055 704 A3



European Patent
Office

LACK OF UNITY OF INVENTION
SHEET B

Application Number
EP 00 30 4092

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

1. Claims: 1-28

Claims 1-28 relate to stabilisers consisting of a blocked mercaptan according to formula 1 and a zinc ionomer (independent claim 16), to PVC compositions comprising the stabiliser (ind. claim 1) and to the use of the stabiliser to improve the water wettability of PVC articles (ind. claim 18).

2. Claims: 29-30

Claims 29-30 relate to a one component stabiliser consisting of a specific complex of a zinc salt with a latent mercaptan.

3. Claims: 31-36

Claims 31-36 relate to a latent mercaptan according to formula 2 (ind. claim 31), PVC zinc ionomer free PVC compositions comprising said mercaptan (ind. claim 32), PVC compositions comprising said mercaptan together with either a specific uracil (ind. claim 34) or a specific pyrrolodiazine dione (ind. claim 35).

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 00 30 4092

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

26-08-2002

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9615186 A		EP 0792317 A1	03-09-1997
		JP 10511994 T	17-11-1998
		WO 9615186 A1	23-05-1996
		US 5880189 A	09-03-1999

US 2002086920 A1	04-07-2002	BR 0002499 A	02-01-2001
		CN 1275591 A	06-12-2000
		EP 1055704 A2	29-11-2000
		JP 2001019817 A	23-01-2001
		AU 716724 B2	02-03-2000
		AU 2126599 A	28-10-1999
		BR 9901026 A	11-04-2000
		EP 0945485 A1	29-09-1999
		JP 11310721 A	09-11-1999
		TW 457272 B	01-10-2001
		US 6232380 B1	15-05-2001
		AU 725806 B2	19-10-2000
		AU 1638499 A	07-10-1999
		AU 699096 A1	19-11-1998
		BR 9803349 A	14-12-1999
		BR 9901192 A	11-04-2000
		CA 2240615 A1	09-01-1999
		CN 1232050 A	20-10-1999
		EP 0890608 A2	13-01-1999
		EP 0945484 A1	29-09-1999
		JP 11310676 A	09-11-1999
		JP 11092592 A	06-04-1999
		NO 983152 A	11-01-1999
		NO 991456 A	27-09-1999
		NZ 330713 A	29-07-1999
		NZ 334126 A	28-10-1999
		PL 327303 A1	18-01-1999
		SG 68055 A1	19-10-1999
		SG 87022 A1	19-03-2002
		SG 80020 A1	17-04-2001
		TW 459009 B	11-10-2001
		US 2002103277 A1	01-08-2002
		ZA 9902294 A	04-10-1999
		ZA 9806049 A	01-02-1999
		AT 197062 T	15-11-2000
		AU 689937 B2	09-04-1998
		AU 3158797 A	30-10-1997
		AU 691448 B2	14-05-1998
		AU 3158897 A	19-02-1998
		AU 682287 B2	25-09-1997
		AU 4816996 A	21-11-1996

EPO FORM P0459

For more details about this annex: see Official Journal of the European Patent Office, No. 12/82